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LIQUID ION EXCHANGE IN FOAM PURIFICATION

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ROBINETTE RESEARCH LABORATORIES, INC.
BERWYN, PENNA.

REPORT

Department of Health, Education and Welfare
Public Health Service
Division of Water Supply and Pollution Control

Final Report
Contract No. PH-86-63-93

LIQUID ION EXCHANGE IN FOAM PURIFICATION

by

Sallie A. Fisher

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TABLE OF CONTENTS

		Page
1.00	Introduction	2
2.00	Description of Materials Screened	3
3.00	Analytical Methods	7
	3.10 Phenol	7
	3.20 Cationic Surfactants	8
	3.30 Anionic Surfactants	9
	3.40 Nonionic Surfactants	10
4.00	Foaming Experiments	10
	4.10 Removal of Alkyl Benzene Sulfonate	11
	4.20 Simultaneous Removal of Phenol and Alkyl Benzene Sulfonate	16
	4.30 Simultaneous Removal of Nonionic Surfactants and Alkyl Benzene Sulfonate	23
5.00	Conclusion	30

LIQUID ION EXCHANGE IN FOAM PURIFICATION

1.00 Introduction

Robinette Research Laboratories, Inc. under Contract No. PH-86-63-93 with the Department of Health, Education and Welfare, Public Health Service, Division of Water Supply and Pollution Control contracted to perform the following work:

/ Screen commercially available water insoluble liquid ion exchange material to determine their efficacy as scavangers for small amounts of organic materials in water using a foaming technique. These materials (anionic, cationic) shall be atomized at low levels into the gas used to produce foam. These materials shall be tested against water containing commonly occuring types of organic contaminants such as phenol, hydrocarbon and all three classes of surfactants (anionic, cationic and nonionic).

A total of 12 water-insoluble liquids containing different types and degrees of ionic functionality were screened for their ability to remove phenols, anionic surfactants and cationic surfactants both alone and in combination with each other. Among the materials tested, the greatest efficiency was found with the use of Duomeen TMO, Tallow 1,3 propylamine diamine monoleate produced by Armour Industrial Chemical Company.

2.00 Description of Materials Screened

The project was set up to investigate the utility of commercially available liquid ion exchange materials as scavangers for organic materials in water. Included in the initial screening were those structures developed specifically as liquid ion exchange resins such as the di- and tri-alkyl amines and the alkyl phosphonic esters and also compounds developed for other purposes which had functionalities with potential usefulness. The criteria used in assembling materials for testing was that they be essentially water-insoluble, that they be liquids at room temperature and that they have one or more polar sites.

The materials tested in various stages of the work are listed in Table 1. All of these materials are commercially available and all are liquids at room temperature. All of them are essentially insoluble in water but, as they are commercial materials, in all likelihood all contain some soluble components. Solubility measurements were made only on those materials that showed the greatest efficiency in the subsequent tests for removal of organic materials from water; namely, Amberlite LA-1, Amberlite LA-2, and Duomeen TMO. For these experiments the agents were bubbled in deionized water at low ratio of deionized water to agent (6 to 1). A vigorous stream of compressed air was used to maintain continuous mixing of agent and water. At the end of one hour the flow of compressed air was stopped and the two phases were separated. The total dissolved solids content

Table 1

MATERIALS INCLUDED IN SCREENING EXPERIMENTS

Trade Name	Supplier	Type
Amberlite LA-1	Rohm & Haas Co.	Alkyl secondary amine
Amberlite LA-2	Rohm & Haas Co.	Branched chain tertiary amine
Armeen DMSD	Armour Chemical	Dimethyl soya amine
Arneel TD	Armour Chemical	Tallow nitrile
Phosgard C-22-R	Monsanto Chemical	Chlorinated phosphate ester
Gafac PE-510	Antara Chemical	Organo phosphate ester
Citroflex A-2	Chas. Pfizer	Acetyl triethyl citrate
Brominol	Abbott Laboratories	Brominated olive oil
Densitol	Abbott Laboratories	Brominated sesame oil
Chlorowax 40	Diamond Alkali	Chlorinated paraffin
Alamine 336	General Mills	Tricaprylamine
Duomeen TMO	Armour Chemical	Tallow 1,3 propylamine diamine monoleate

of the aqueous phase was determined and the organic phase was returned to the system to be bubbled again with a fresh portion of deionized water. This process was repeated four times with each agent. Results of the total dissolved solids determination are tabulated in Table 2.

It is obvious from these results that these commercial products all contain some soluble material. In the case of the Amberlite LA-1, it is presumed from the results that this soluble material is in the form of an impurity which may be removed from the agent by extraction with water. With the Amberlite LA-2 and the Duomeen TMO the soluble component is apparently a major portion of the commercial product. Hence, they do not lend themselves to purification by extraction with water. In subsequent experiments the solubility of these agents in water was monitered at frequent intervals by determination of total dissolved solids under the conditions of test.

Table 2

WATER EXTRACTABLE CONTENT OF VARIOUS AGENTS

	Per Cent Extracted[(a)]		
	Amberlite LA-1	Amberlite LA-2	Duomeen TMO
1st Extraction	2.94	0.28	0.38
2nd Extraction	0.24	0.056	0.24
3rd Extraction	0.14	0.24	0.056
4th Extraction	0.086	0.15	0.26

(a) 50 grams of agent bubbled vigorous with successive 300 ml. portions of deionized water. Per cent extracted calculated from TDS of water used.

3.00 Analytical Methods

In view of the commercial nature of materials selected for initial screening and, as noted above, the fact that some of them were slightly soluble in water, the analytical methods selected for determination of phenols, for anionic surfactants and for cationic surfactants were tested to determine whether the agents plus water produced a solution that would in any way interfere in the analysis. Results obtained are discussed by individual contaminant below.

3.10 Phenol

The 4-amino antipyrine method for phenol using a filter photometer as described in the "Standard Methods for the Examination of Water, Sewage and Industrial Wastes, Tenth Addition", page 339, was used for the determination of phenol. Possible interference of the agents in Table 1 was tested by shaking 100 milliliters of deionized water with 0.5 grams of each agent at 25°C. for 30 minutes. The agent was then allowed to stand in contact with the water for an additional hour before removal of a sample for phenol analysis. Fifty milliliter portions of the water so-treated gave readings which were indistinguishable from a deionized water blank carried through the same procedure in each case.

Similar equilibration runs were made with a solution containing one part per million phenol. Both of the phosphorus-containing compounds (Gafac PE510 and Phosgard C-22-R) produced a slight reduction in phenol concentration of the solution under these conditions. A higher level of phenol

removal was noted with the dimethyl soya amine (Armeen DMSD). The combination of phenol and Arneel TD produced erratic results which indicated that some impurity capable of reacting with the analytical agent was present in this case.

3.20 Cationic Surfactants

A solution of (diisobutylphenoxyethoxyethyl) dimethyl benzylammonium chloride (Hyamine 1622, produced by the Rohm & Haas Company) was used as a prototype cationic surfactant. It was estimated by an adaptation of the method of Auerbach (Industrial and Engineering Chemistry, Anal. Ed. 16, 739 (1944)) as further modified by Cucci (Soap, 24, 129, (1948)) to use chloroform as the extractant for the bromophenol blue complex. In this procedure a standard solution of Aerosol OT (sodium di-(2-ethylhexyl) sulfosuccinate, produced by American Cyanamid Corporation.) was used as the anionic titrant. The dissappearance of blue color of the bromophenol blue complex in the chloroform was used as the end point and gave excellent reproducibility in the 10 to 100 part per million range.

As in the previous experiments, the interference of the agents listed in Table 1 was first tested by analysis of deionized water which had been shaken with 0.5% of their weight of the agent. In this test both the Phosgard C-22-R and the Gafac PE 510 showed sufficient solubility either to require a back titration with cationic agent(Hyamine 1622) or to form an emulsion with the chloroform in the analysis.

When these tests were repeated using solutions containing known concentrations of the prototype cationic material (Hyamine 1622) only the Arneel TD

and the Citroflex A-2 showed no interference in the reaction. The Phosgard C-22-R, Brominol and Densitol results all indicated that they had reacted with Hyamine 1622 in some fashion either to remove it from the aqueous phase or otherwise decrease the amount of Aerosol OT necessary to titrate it. With the Amberlite LA-1, Amberlite LA-2 and Armeen DMSD, which are cationic in themselves, the consumption of Aerosol OT was increased. Therefore, it is assumed that while they are not sufficiently cationic to react with bromophenol blue and produce a color in the chloroform layer, they are sufficiently cationic to react with Aerosol OT. In all subsequent work with these and other cationic agents an agent blank was used as a portion of the analytical procedure.

3.30 Anionic Surfactants

Anionic surfactants were determined by reversing the method used for the determination of cationic surfactants. In this procedure an excess of Hyamine 1622 was added to the solution to be analyzed and the unreacted excess then titrated with Aerosol OT. The procedure was tested using a sodium dodecylbenzene sulfonate (Santomerse 3) as the prototype anionic surfactant. Direct correlation between the amount of this material present in solution and the decrease in the back titration with Aerosol OT could be obtained in the range of 10 to 100 parts per million of Santomerse 3.

When this method was applied to agent-treated samples, interference occurred with the same materials as in the cationic surfactant titration. All of the agents which were cationic required larger amounts of Aerosol OT in the back titration. The phosphate esters produced emulsions in the titration

which broke so slowly that it was difficult to evaluate the color of the two layers. Some tendency toward the removal of anionic materials was noted in the samples treated with Chlorowax 40 and Arneel TD.

3.40 Nonionic Surfactants

Combinations of nonionic surfactants with alkyl benzene sulfonates were analyzed in the latter stages of the program. In all such cases, the total dissolved solids content of the treated solutions were determined and the total value obtained was corrected for the amounts of the other constituents determined by the methods above to give, by difference, the amount of nonionic surfactant.

4.00 Foaming Experiments

Various modifications of foaming baths were tried during the contract period to permit the introduction of small amounts of liquids with air. For most of the small scale experiments the agent was introduced via a sparger which had a nylon taffeta diaphragm. This sparger resembles a filter stick with a piece of nylon used in place of the usual sintered glass plate. Such an apparatus produced bubbles of small size with a very low pressure drop across the diaphragm. The agent to be tested was applied directly to the nylon and blown in with the air. The diaphragm was used once and subsequently discarded, a procedure which greatly simplified cleaning the apparatus. Such an apparatus produced a suitable foam of microbubbles with a pressure differential as low as 6 centimeters of mercury.

In larger vessels a series of such spargers was first used. Some difficulty in getting good mixing at the bottom was noted, however. A further

modification of the design to set the spargers flush in the bottom of the test vessel was made to provide a better patterned spray of droplets into the apparatus.

4.10 Removal of Alkyl Benzene Sulfonate

Sodium dodecyl benzene sulfonate (Santomerse 3) was used as the prototype anionic surfactant. In initial experiments, standardized solutions of Santomerse 3 were tested with all of the agents listed in Table 1. The cationic materials in the group; namely, Amberlite LA-1, Amberlite LA-2, Alamine 336, Armeen DMSD, and Duomeen TMO all showed an ability to remove alkyl benzene sulfonate from solution in initial experiments. With these cationic materials the foam initially generated with the alkyl benzene sulfonate completely dissappeared during the course of a 30 minute test period. An analysis of the water treated showed some removal of the ABS in all cases.

These five cationic agents were investigated in greater detail to develop information concerning their relative efficiencies. For these experiments high concentrations of alkyl benzene sulfonate (200 to 400 ppm) were used in the bath. Agents were introduced by the passage of an air stream through nylon diaphragms in the apparatus described above. The bath was analyzed for residual alkyl benzene sulfonate at the end of a 30 minute foaming period in each case. Results, shown in Table 3, indicate that the two Amberlite materials, the Alamine and the Duomeen TMO were approximately equal in efficiency for removal of alkyl benzene sulfonate. Further, the efficiency

Table 3

REMOVAL OF ABS FROM WATER BY
VARIOUS AGENTS

Agent	Initial ABS Conc.	Ratio Bath/Agent	% ABS Removal[a]
Amberlite LA-1	200 ppm	200	75
Amberlite LA-1	400 ppm	200	74
Alamine 336	200 ppm	200	70
Alamine 336	400 ppm	200	75
Armeen DMSD	200 ppm	200	50
Armeen DMSD	400 ppm	200	34
Amberlite LA-2	200 ppm	200	83
Duomeen TMO	200 ppm	200	75

(a) 30 minutes foaming

of the removal did not decrease at higher concentrations of ABS indicating that the efficiency was more likely governed by the contact between agent and solution.

Additional experiments with the same agents at higher ratios of bath to agent are reported in Table 4. In these experiments the alkyl benzene sulfonate concentration was maintained at the 200 ppm level. It will be noted that the efficiency of removal has not been seriously diminished by a four fold increase in the bath volume. In the data reported in Table 4, that reported under the Column "Agent Blank" represents an analysis wherein the blank for the titration has been a water solution through which an equivalent amount of agent has been passed using the same technique as in the samples. In that reported under "DI Blank" untreated deionized water has been used as the blank. It will be noted that the use of the deionized water produces a more logical set of numbers.

It is known, of course, that some of these materials do contain a soluble constituent. A comparison of the total dissolved solids content of samples after treatment with the various cationic agents with their apparent alkyl benzene sulfonate concentrations as obtained by titration is given in Table 5. In this series of samples, as in all of those for which results have been previously reported, the alkyl benzene sulfonate was dissolved in deionized water. Hence the total dissolved solids must consist of residual alkyl benzene sulfonate plus dissolved agent. It will be noted in Table 5 that in every case the total dissolved solids is higher than the apparent alkyl

Table 4

REMOVAL OF ABS BY VARIOUS AGENTS

AT DIFFERENT RATIOS OF AGENT TO BATH

Agent	Initial ABS Conc.	Ratio Bath/Agent	% ABS Removal(a)	
			Agent Blank	DI Blank
Amberlite LA-1	200	200	75	100
Amberlite LA-1	200	400	80	87
Amberlite LA-1	200	800	82	83
Amberlite LA-2	200	200	83	92
Amberlite LA-2	200	400	87	90
Amberlite LA-2	200	800	87	87
Alamine 336	200	200	75	92
Alamine 336	200	400	75	75
Alamine 336	200	800	77	77
Armeen DMSD	200	200	50	100
Armeen DMSD	200	400	33	90
Duomeen TMO	200	200	75	97
Duomeen TMO	200	400	83	93
Duomeen TMO	200	800	83	93

(a) 30 minutes foaming

Table 5

COMPARISON OF TOTAL DISSOLVED SOLIDS WITH ABS CONCENTRATION

Agent	Ratio Water/Agent	g. Agent Used	ABS ppm(a)	TDS ppm
Amberlite LA-1	500	2.0	34	150
Amberlite LA-1	400	0.5	40	52
Amberlite LA-2	500	2.0	30	47
Amberlite LA-2	400	0.5	26	44
Alamine 336	500	2.0	68	490
Alamine 336	400	0.5	50	64
Duomeen TMO	500	2.0	25	94
Duomeen TMO	400	0.5	34	36

(a) By Titration

benzene sulfonate concentration. Further, the larger the amount of agent used in the experiment the higher the total dissolved solids content. In all cases these solutions contain an initial ABS concentration of 200 ppm.

A further check on the correlation between the ABS concentration measured by titration and the total dissolved solids was made by determining the total dissolved solids in both the treated ABS containing samples and in deionized water treated with the same amount of agent under the same conditions. These results shown in Table 6 indicate that a correction of the total dissolved solids for the amount of dissolved agent produces a good correlation with the value for ABS obtained by titration.

As will be noted in Tables 4, 5, & 6, all of the cationic agents tested showed an ability to remove alkyl benzene sulfonate from water solutions. Work with the Armeen DMSD, however, was discontinued at this point because of its great tendency to form emulsions in solutions containing alkyl benzene sulfonate.

4.20 Simultaneous Removal of Phenol and Alkyl Benzene Sulfonate

In early experiments the removal of phenol from a solution containing tridecyloxypoly (ethyleneoxy) ethanol (Emulphogene BC-720) were attempted. The Emulphogene BC-720, which is a nonionic surfactant, was added to the phenol solutions to produce foam. This was in line with the original concept of the removal of impurities by collection in the foam above the water. These experiments, in which all of the agents in Table 1 were tried for phenol removal, were negative in that no phenol removal was accomplished.

Table 6

COMPARISON OF TITRATION METHOD WITH TOTAL DISSOLVED SOLIDS

Agent	Total Solids (ppm)		Residual ABS Conc. (ppm)		
	Sample[a]	Blank[b]	From TDS[c]	By Titration	
				Agent Blank	DI Blank
Amberlite LA-1	52	12	40	40	26
Amberlite LA-2	44	4	40	26	20
Alamine 336	64	4	60	50	50
Duomeen TMO	36	<1	36	34	14
Armeen DMSD	24	8	16	134	20

(a) 200 ppm. ABS bubbled at bath ratio of 400/1 for 30 min.

(b) Agent in deionized water at ratio of 400/1.

(c) ppm Solids in sample - ppm solids in blank.

Further, the presence of nonionic surfactant produced emulsions with many of the agents tried.

Subsequent work in which alkyl benzene sulfonate was removed from solution indicated that foam was not essential to the efficiency of the process. Indeed, the most efficient agents for the removal of alkyl benzene sulfonate acted as defoamers and collected the impurity in small liquid droplets at the top of the water.

In a new set of experiments the removal of phenol from deionized water was attempted without production of foam by any agent. In these experiments a solution containing 10 ppm of phenol was bubbled with varying amounts of the four agents (Amberlite LA-1, Amberlite LA-2, Duomeen TMO and Alamine 336) that had shown promise for the removal of alkyl benzene sulfonate. At the two ratios of agent test water used (see Table 7) only slight removal of phenol at the end of 30 minutes bubbling was noted in any case. The agents were applied in these experiments using the same technique of forcing air through a nylon diaphragm wet with the agent described in the previous sections.

In a further series of experiments the removal of phenol from water containing alkyl benzene sulfonate was compared with the removal of this impurity from deionized water. These experiments (Table 8) indicated that some removal of phenol did occur with the alkyl benzene sulfonate and that it was possible that the efficiency was increased by the presence of the

Table 7

PHENOL REMOVAL BY VARIOUS AMINES

Agent	Ratio Water/Agent	Phenol Conc. (ppm) Initial	Final[a]
Amberlite LA-1	200	10	9
Amberlite LA-1	500	10	10
Amberlite LA-2	200	10	9
Amberlite LA-2	500	10	8
Alamine 336	200	10	10
Alamine 336	500	10	9.5
Duomeen TMO	200	10	8
Duomeen TMO	500	10	8.5

(a) After 30 minutes bubbling

Table 8

SIMULTANEOUS REMOVAL OF PHENOL AND ABS

Agent	Amberlite LA-1			Amberlite LA-2			Duomeen TMO		
Ratio, Water/Agent	200	200	200	200	200	200	200	200	200
Phenol Conc. (ppm)									
Initial	10	0	10	10	0	10	10	0	10
Final[(a)]	9	0	5	9	0	8	8	0	8
ABS Conc. (ppm)									
Initial	0	200	200	0	200	200	0	200	200
Final[(a)]	0	50	60	0	34	25	0	50	35

(a) After 30 minutes bubbling

second contaminent. Additional experiments with larger amounts of both phenol and alkyl benzene sulfonate (Table 9) confirms the fact that phenol is being removed with the alkyl benzene sulfonate. This removal, however, appears to be an equilibrium value with the amount left in solution being very closely proportional to the amount present initially. From these results the Amberlite LA-1 and the Duomeen TMO show the greatest capacity for the removal of phenol from solutions containing alkyl benzene sulfonate.

Table 9

EFFECT OF AGENT LEVEL ON REMOVAL OF PHENOL PLUS ABS

Agent	Amberlite LA-1		Amberlite LA-2		Duomeen TMO	
Ratio, Water/Agent	200	500	200	500	200	500
Phenol Conc.(ppm)						
Initial	10	20	10	20	10	20
Final[(a)]	5	13	8	18	8	14
ABS Conc.(ppm)						
Initial	200	500	200	500	200	500
Final[(a)]	60	140	25	114	35	54

(a) After 30 minutes bubbling

4.30 Simultaneous Removal of Nonionic Surfactants & Alkyl Benzene Sulfonate

Of the many available types of nonionic surfactants, two have been selected for screening studies. These were a polyoxyethylated tert-octylphenol with 9 to 10 moles of ethylene oxide per mole (Triton X-100 produced by the Rohm & Haas Company) and a polyoxyethylated lauryl alcohol (Lipal LA-7 produced by Drew Chemical Co.). Selection of these materials was based on a desire to have both an aryl and an alkyl representative included in the experiments. Choice of one example in each class was made on the basis of water solubility and on the basis of moderate foaming characteristics so that higher concentrations of these materials might be employed without producing a room full of foam.

Removal of these two nonionic materials by the various agents was investigated in solution in combination with alkyl benzene sulfonate. Only the two agents which had shown the greatest efficiency in the foregoing experiments; namely, Amberlite LA-1 and Duomeen TMO, were tested in this series of experiments.

In the first set of experiments, solutions of alkyl benzene sulfonate (Santomerse 3) and Triton X-100 were treated with these two cationic agents at two different ratios of bath to agent for total contact times of 30 and of 60 minutes. The treated water was then analyzed for alkyl benzene sulfonate concentration by titration and its total dissolved and suspended solids content was also determined. Results (Table 10) show that the apparent alkyl benzene sulfonate removal has been much more efficient with the Duomeen TMO than

Table 10

SIMULTANEOUS REMOVAL OF ABS

AND POLYOXYETHYLATED TERT-OCTYLPHENOL[a]

FROM DEIONIZED WATER

Agent Tested	Ratio Agent/Bath	Contact Time (min)	ABS Conc. (ppm)		Nonionic Conc. (ppm)	
			Initial	Final[b]	Initial	Final[b]
LA-1	1-1000	30	150	92	100	200
LA-1	1-1000	60	150	87	100	217
LA-1	1-2000	30	150	75	100	293
LA-1	1-2000	60	150	75	100	245
TMO	1-1000	30	150	12	100	386
TMO	1-1000	60	150	7.5	100	417
TMO	1-2000	30	150	60	100	362
TMO	1-2000	60	150	52	100	348

(a) Triton X-100, produced by Rohm & Haas Company

(b) ABS Conc. obtained by titration. "Nonionic" conc. from total solids minus residual ABS conc.

with the Amberlite LA-1. However, when the total dissolved and suspended solids content of the solution is determined the apparent nonionic surfactant concentration, calculated by subtracting the residual alkyl benzene concentration from the total solids is in all cases higher than the initial concentration. Thus it is apparent that while the alkyl benzene sulfonate reacts with the two agents in the presence of nonionic surfactants to form a complex which no longer takes part in the normal titration reaction, the nonionic surfactant keeps the tiny droplets of agent-ABS complex suspended in the water so that they do not collect at the top as in previous experiments.

Similar experiments with solutions of Lipal LA-7 and Santomerse 3 were carried out. Data, shown in Table 11, again indicate the greater efficiency of the Duomeen TMO as an agent for the removal of alkyl benzene sulfonate. The apparent nonionic concentration, when Amberlite LA-1 is used as the scavenging agent, is less than the initial concentration, indicating that the tendency of the alkyl ethylene oxide derivative to hold the ABS-agent complex in suspension is considerably less than that of the aryl compound. In the case of the Duomeen TMO, the total solids measured at short contact times are higher than the original nonionic concentration. However, this concentration decreases with longer application of air to the system indicating that the agent complex slowly separates from the initial suspension.

All of these experiments as well as all of those in preceeding sections had involved the use of synthetic solutions prepared in deionized water. While this represents a convenient case for the analyst it also represents one far

Table 11

SIMULTANEOUS REMOVAL OF ABS

AND POLYOXYETHYLATED LAURYL ALCOHOL[a]

FROM DEIONIZED WATER

Agent Tested	Ratio Agent/Bath	Contact Time (min)	ABS Conc. (ppm)		Nonionic Conc. (ppm)	
			Initial	Final[b]	Initial	Final[b]
LA-1	1-1000	30	150	105	100	91
LA-1	1-1000	60	150	93	100	69
LA-1	1-2000	30	150	105	100	87
LA-1	1-2000	60	150	100	100	90
TMO	1-1000	30	150	23	100	155
TMO	1-1000	60	150	15	100	27
TMO	1-2000	30	150	53	100	119
TMO	1-2000	60	150	63	100	109

(a) Lipal LA-7, produced by Drew Chemical

(b) ABS Concentration by titration. Nonionic from total solids minus ABS Concentration.

removed from reality. Hence, additional experiments were conducted using solutions of the nonionic agents and Santomerse in Philadelphia Suburban tap water.

These experiments in tap water were carried out in the same manner as the previous experiments except that a solution of alkyl benzene sulfonate without nonionic was included in the series. Results for the series where Triton X-100 were used as the nonionic as given in Table 12. One would conclude from comparing this series with the data in Table 10 that the use of tap water has made no major difference in the efficiency of scavanging mixtures of nonionic surfactants and alkyl benzene sulfonate. However, the Santomerse alone in the tap water shows a tendency to form a suspension of agent-complex in tap water which gives rise to a total solids content much higher than that previously noted when this agent was run in deionized water (Tables 5 and 6).

Similar data for solutions of Lipal LA-7 and Santomerse 3 in tap water are given in Table 13. Here again the results from deionized water (Table 11) and tap water are almost identical.

The large amount of agent which remained suspended in the water when nonionic surfactants were present was naturally a cause for concern. One series of runs was made to determine whether a diluent might be added to the system to serve as an emulsion-breaker. This run was made with Duomeen TMO dissolved in petroleum ether. The solution of TMO in petroleum ether was aspirated into the air stream and the analysis of the solution was made in the same manner as previously described. The results of these experiments,

Table 12

SIMULTANEOUS REMOVAL OF ABS

AND POLYOXYETHYLATED TERT-OCTYLPHENOL[a]

FROM TAP WATER[b]

Agent Tested	Ratio Agent/Bath	Contact Time (min)	ABS Conc. (ppm)		Nonionic Conc. (ppm)	
			Initial	Final[c]	Initial	Final[c]
LA-1	1-1000	30	150	84	0	70
LA-1	1-1000	60	150	81	0	37
LA-1	1-1000	30	150	89	100	179
LA-1	1-1000	60	150	91	100	159
LA-1	1-2000	30	150	102	0	54
LA-1	1-2000	60	150	100	0	74
LA-1	1-2000	30	150	106	100	154
LA-1	1-2000	60	150	109	100	203
TMO	1-1000	30	150	26	0	90
TMO	1-1000	60	150	33	0	109
TMO	1-1[illegible]	30	150	63	100	293
TMO	1-1000	60	150	18	100	402
TMO	1-2000	30	150	48	0	40
TMO	1-2000	60	150	36	0	108
TMO	1-2000	30	150	69	100	193
TMO	1-2000	60	150	84	100	240

(a) Triton X-100 produced by the Rohm & Haas Company
(b) Philadelphia Suburban Water, 98 ppm TDS
(c) ABS Conc. by titration. "Nonionic" from TDS minus (ABS+TDS of water).

Table 13

SIMULTANEOUS REMOVAL OF ABS

AND POLYOXYETHYLATED LAURYL ALCOHOL[a]

FROM TAP WATER[b]

Agent Tested	Ratio Agent/Bath	Contact Time (min)	ABS Conc. (ppm)		Nonionic Conc. (ppm)	
			Initial	Final[c]	Initial	Final[c]
LA-1	1-1000	30	150	105	100	83
LA-1	1-1000	60	150	98	100	82
LA-1	1-2000	30	150	112	100	96
LA-1	1-2000	60	150	107	100	121
TMO	1-1000	30	150	38	100	108
TMO	1-1000	60	150	27	100	137
TMO	1-2000	30	150	57	100	125
TMO	1-2000	60	150	72	100	128

(a) Lipal LA-7, produced by Drew Chemical.

(b) Philadelphia Suburban Water, 98 ppm TDS.

(c) ABS Conc. by titration, "Nonionic" from TDS minus (ABS plus TDS of water).

shown in Table 14, indicate that the overall efficiency of the process has been greatly improved by the dilution of the Duomeen TMO with petroleum ether. Not only has the formation of suspensions which gives rise to high solids been completely eliminated but there is evidence that with the added solvent the nonionic concentration in the solution is drastically reduced. Of interest perhaps are the solutions in which only petroleum ether was applied. Here the apparent nonionic concentration is very low. However, in these solutions foam production was high and it is assumed that a large portion of the surfactant was present in the foam layer above the solution which was drawn for analysis.

5.00 Conclusion

The above program was started as a screening program to evaluate the utility of liquid ion exchange materials as scavangers for water purification. Use of the liquid amines, particularly Alamine 336, has been proposed from time to time as a commercial process for the removal of alkyl benzene sulfonate. It is obvious from the foregoing results that it is not the optimum structure for such applications. Compounds with dual amine functionality in a single molecule show greater efficiency.

The selection of Duomeen TMO, a tallow 1, 3 propylene diamine monoleate for the present study was a matter of chance rather than scientific acuity. This material is only one of a whole family of such materials, some of which commercially available, and others of which could be synthesized. Only one other member of the series, Duomeen C, a cocoa 1, 3 propylene diamine was tried in the procedure. This member of the series is both too

Table 14

SIMULTANEOUS REMOVAL OF ABS
AND NONIONIC SURFACTS WITH
DUOMEEN TMO IN PETROLEUM ETHER

Agent Used g.TMQ	g.P.E.	Vol. Water (ml)	Time Min.	ABS Conc.(ppm) Initial	Final(a)	Nonionic Used	Nonionic Conc. (ppm) Initial	Final(b)
0	4.5	1000	30	150	145	Triton X-100	100	7
0	4.5	1000	60	150	141	"	100	21
0.5	4.5	1000	30	150	22	"	100	66
0.5	4.5	1000	60	150	12	"	100	62
0.5	0	1000	30	150	60	"	100	362
0.5	0	1000	60	150	52	"	100	348
0	4.5	1000	30	150	132	Lipal LA-7	100	10
0	4.5	1000	60	150	132	"	100	8
0.5	4.5	1000	30	150	45	"	100	47
0.5	4.5	1000	60	150	16	"	100	16
0.5	0	1000	30	150	53	"	100	119
0.5	0	1000	60	150	63	"	100	109

(a) By titration

(b) Total dissolved solids minus ABS Conc.

soluble in water and too prone to forming emulsions for use in such a process. It is, however, possible that a better material than the Duomeen TMO exists in the series.

Aspiration of these materials into the air stream in a diluted form also is favorably indicated. The diluent prevents the formation of a suspension of agent droplets in the water, particularly when nonionic surfactants are present. Further, it appears to improve the contact between agent and solution and provides for a greater efficiency when a given amount of agent is applied to a given bath volume. Petroleum ether is the only solvent which has been used in such an application. It was selected primarily because of the ease of solubility of the particular agent, Duomeen TMO, which was being used in the preliminary experiments.

There is some evidence that while the amine agents will not remove phenol and nonionic materials in the absence of alkyl benzene sulfonate, these materials may be removed along with the anionic agents. No investigation of phenol removal has been made with the diluted agent and it is possible that greater efficiencies than those reported herein will be encountered in such a system.